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HgCdTe FABRICATION USING DIRECTED ENERGY TECHNIQUES

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20. The final result is a single crystal film of $Hg_{(1-x)}Cd_xTe$, 30 microns thick and 0.5 inch square, with a compositional variation of x less than ± 0.0007 . Films of up to 20 microns thick, 1 inch o.d., single crystal (but twinned) CdTe were produced by the first process. These faceted films were smoothed without change of surface stoichiometry or structure by the second process. Evaporation of HgTe at less 0.5 atm Hg overpressure onto the CdTe film produced the final result on mica or quartz substrates. Electron mobility at 77°K was as high as $1.5 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ in the final samples. ←

100,000 $\text{cm}^2/\text{V}\cdot\text{s}$

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TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
FOREWORD	1
SUMMARY	2
1 INTRODUCTION	3
1.1 Purpose - Long-Term Objective	3
1.2 Technical Considerations	3
1.3 General Method	3
1.4 Technical Results and Conclusions	5
2 TECHNICAL CONSIDERATIONS: DEPOSITION OF SINGLE-CRYSTAL CdTe FILMS	6
2.1 Objective	6
2.2 Hot Wall Epitaxy Process Description	6
2.3 Vacuum Systems for HWE Deposition of CdTe	7
2.4 Hot Wall Epitaxy Furnace	7
2.5 Heteroepitaxial Growth of CdTe on Mica	10
2.6 Characterization of CdTe Films on Mica	14
2.7 Films Deposited on Other Substrates	17
3 TECHNICAL CONSIDERATIONS: VAPOR EXCHANGE OF CdTe TO FORM HgCdTe	24
3.1 Objective	24
3.2 EDICT Process Description	24
3.3 EDICT Ampoules and Furnace	25
3.4 EDICT Experiments	27
3.5 Characterization of HgCdTe Films	30
4 TECHNICAL CONSIDERATIONS: PULSED ELECTRON BEAM SURFACE PROCESSING	38
4.1 Objectives	38
4.2 Method	38
4.3 Surface Polishing	38
4.4 Crystal Structure	41
REFERENCES	43

LIST OF FIGURES

<u>Figure</u>		
2-1 The Vacuum System for Hot Wall Epitaxy Deposition of CdTe Films (Top) and Initial Furnace (Bottom)	8	
2-2 Hot Wall Furnace With Enclosed Source for Evaporation of CdTe	9	
2-3 Time-Temperature Cycles of the Source and Substrate	12	
2-4 Source and Substrate Temperature Necessary to Give Single Crystal CdTe Films on Mica	13	
2-5 SEM Photomicrograph Showing CdTe Nuclei	15	
2-6 CdTe Film (5 microns Thick) Deposited on Mica	16	
2-7 Back Reflection Laue Pattern From CdTe Film on Muscovite Mica (Specimen M81)	18	
3-1 Schematic of Vapor Exchange Apparatus (at NERC)	26	
3-2 A Heat Pipe is Placed Inside The EDICT Furnace to Ensure Growth in Thermodynamic Equilibrium	28	
3-3 Fourier Transform Reflectance Spectroscopy Measurements Taken on a HgCdTe/Mica Sample and a Bare Mica Substrate	31	
3-4 Compositional Uniformity of 0.2190 +0.00067 Across a 1.2x1.2 cm Area Measured With the Fourier Transform Spectrometer Which has a Precision Limit for Resolving X of +0.00050	33	
3-5(a) Laue X-ray Pattern of a Single Crystal CdTe Film on Mica	35	
3-5(b) Laue X-ray Pattern of the Same Sample Shown Above After the EDICT Process Showing Improved Crystalline Quality	35	
3-6(a) Laue X-ray Pattern Taken on a Bulk CdTe Wafer	36	
3-6(b) Laue X-ray Pattern Taken on the Same Sample as (a), but After the EDICT Process	36	
4-1 Electron Energy Spectrum of Beam Used to Process CdTe	39	
4-2 HWE Deposited CdTe Film on Mica Irradiated by Pulsed Electron Beam in 5 mm Square Area	40	
4-3 HWE Deposited CdTe Film Before (Top) and After (Bottom) Pulsed Electron Beam Irradiation, Showing in SEM Microphotograph Surface Polishing by Melting	42	

FOREWORD

The work reported in this document was performed in part at Spire Corporation, Bedford, Massachusetts, and in part at New England Research Center, Inc., Sudbury, Massachusetts, under contract MDA 903-79-C-0434, DARPA order number 3800. The contract monitor is Mr. Sven Roosild.

The program manager at Spire is Dr. Robert Wolfson. The principal investigator at Spire is Dr. Anton Greenwald, who is in charge of pulsed electron beam processing and ion implantation studies. The program manager at NERC is Dr. Theodore Wong. The principal investigator at NERC is Dr. John Miles, who is in charge of the epitaxial deposition and vapor exchange processes.

The report of the main subcontractor, NERC, is included in Sections 1, 2 and 3. Work performed at Spire during this period is described in Section 4.

SUMMARY

The goal of this research is to produce large-area, single-crystal HgCdTe material for infrared detectors. The approach is (1) to evaporate CdTe films onto insulating substrates for epitaxial crystal growth; (2) to heat the film with a pulsed, directed energy beam to reduce defect concentration and improve surface morphology; and (3) to convert the material to HgCdTe by vapor-exchange with HgTe.

Single crystal films of $Hg_{(1-x)}Cd_xTe$ up to 30 microns thick were fabricated on 1.2 x 1.2 cm mica substrates. Excellent compositional uniformity was achieved, with the variation in x less than ± 0.0007 . The electron mobility in this material was as high as $1.5 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ at 77°K . Good reproducibility has been demonstrated with the result that $HgCdTe$ films can be grown with predictable thickness and composition.

The surface morphology of the CdTe films as deposited, step (1) above, is faceted. It has been shown, as noted in step (2) above, that pulsed electron beam processing can melt and polish this surface without degradation of crystal structure or compositional uniformity. The final surface is suitable for making devices.

The technical tasks for this program were completed ahead of schedule. Initial objectives were achieved.

SECTION 1 INTRODUCTION

1.1 PURPOSE - LONG-TERM OBJECTIVE

The overall purpose of this program is to grow large size single crystal HgCdTe suitable for use in large scale detector arrays. For this purpose, the material must have the following properties:

- Uniformity of composition ($X \leq .003$)
- Dimension of 1" or greater
- Near intrinsic purity
- Freedom from residual stress and surface defects
- Large scale production capability

1.2 TECHNICAL CONSIDERATIONS

There are two main problems which prevent present melt growth methods from satisfying all the above criteria simultaneously. The first of these problems is the high vapor pressure of mercury associated with the pseudobinary phase for molten $Hg_{(1-x)}Cd_xTe$. This problem places limits on the dimension of the ampoule in which the crystals may be grown. The second major problem is the wide separation of the liquidus and solidus in the pseudobinary phase diagram which makes it very difficult to obtain a uniform composition across a large specimen.

The methods used in the program overcome these two problems without introducing any other insuperable problems as indicated in the next section.

1.3 GENERAL METHOD

The method used in this program attains the desired end of large area, uniform single crystal HgCdTe films in two steps. The first step is to grow heteroepitaxially large single-crystal films of CdTe on foreign substrates by the Hot Wall Epitaxial (HWE) technique. The second step is transformation from single crystal CdTe film to single crystal HgCdTe film by a process of vapor growth and solid state diffusion known as EDICT (Evaporation and Diffusion at Constant Temperature).

This two-step method has a number of advantages over other methods of growing large area HgCdTe single-crystal specimens. First, the film thickness is determined by the deposition of the CdTe in the first step, whereas the critical HgCd ratio is

determined by the second step. This allows the critical parameters to be separately optimized. Secondly, since all processes take place at relatively low temperatures, the excessive mercury pressure that plagues most high-temperature melt-growth processes is not a problem. In fact, this method takes advantage of the volatility of components and grows from the vapor phase. Scaling up of the specimen dimensions is rather straightforward relative to other melt-growth methods which are all limited by the 1/2" ampoule dimension as a result of high mercury pressures. Thirdly, segregation problems which limit uniformity of composition in melt-grown HgCdTe do not exist in this method because melting is not required here. Furthermore, since HgCdTe is grown directly in a thin CdTe film, no compositional gradient occurs. Thus, exceptionally uniform composition should result both across and normal to the film surface. Finally, both the Hot Wall Heteroepitaxy and the EDICT process are vapor-growth methods where the emphasis is put on the growth of epitaxial layers under conditions as near as possible to thermodynamic equilibrium, resulting in thin films of bulk quality and crystalline perfection.

An additional step is necessary for processing the CdTe film after HWE deposition. The growth morphology of the as-deposited film is faceted, with surface relief greater than one micron. The surface features remain essentially unchanged after EDICT conversion to HgCdTe. Polishing a thin film is difficult and costly. However, rapid melt/quenching by irradiation with a pulsed electron beam produces a superior surface finish. As the surface cools, epitaxial crystal growth prevents degradation of structure. The surface is typically at a high temperature for only one microsecond, and this minimizes outdiffusion of Cadmium. The process is fast, noncontaminating, inexpensive, and amenable to large-scale manufacture.

Four substrate materials have been used for the deposition of CdTe films; namely, muscovite mica, single-crystal quartz, sapphire and silicon. The reasons for the choice of these particular materials were as follows:

1. Mica is a readily available, cheap substrate material which has a facile cleavage plane. This allows the use of perfectly oriented substrate which is uncontaminated if carefully used. It is a cheap and easy substrate to use in quick repetitive experiments to obtain data for the optimization of deposition parameters. Its expansion coefficient normal to the cleavage plane is $8.5 \times 10^{-6}/^{\circ}\text{C}$ compared with 5.5×10^{-6} for CdTe. It may be used at temperatures

up to 550°C, which is higher than the operating temperature at which the vapor transport experiments are performed. It is therefore a possible substrate for later practical use and not just a convenient substrate for calibration of the apparatus.

2. Crystalline quartz is a readily available, easily cleanable substrate. It is the crystal form of fused silica, which is known to be innocuous to HgCdTe at higher use temperatures during bulk growth. It can be obtained in oriented-polished form. It was therefore chosen as a noncontaminating substrate.
3. Sapphire is a substrate commonly used with bulk HgCdTe and has an excellent thermal expansion match. It is a clean, noncontaminating substrate and may be obtained oriented with its surface normal to the hexagonal c-axis. However, it is difficult to obtain oriented to better than 1°.
4. Silicon is cheap and easily obtainable in very pure form, oriented to the desired crystal plane. It must be protected from Te vapor at the temperature at which the vapor transport experiments are performed and hence needs a thin layer of oxide on the surface. Silicon is thus most suited for experiments in graphoepitaxy.

1.4 TECHNICAL RESULTS AND CONCLUSIONS

Results on this program have confirmed the feasibility of combining the HWE and EDICT methods to grow large single-crystal HgCdTe films. The major accomplishments to date are listed below:

- Heteroepitaxial single-crystal CdTe films 2.5 cm in diameter have been grown by the HWE technique.
- Single-crystal HgCdTe films have been produced by means of a subsequent EDICT treatment of these CdTe films.
- Excellent compositional uniformity has been achieved in $Hg_{(1-x)}Cd_xTe$ films with compositional variation in X of less than ± 0.00067 over a nominal area of 1.2 cm x 1.2 cm as determined by spectral cutoffs at 77°K.
- Electron mobility as high as $1.5 \times 10^5 \text{ cm}^2/\text{V-s}$ at 77°K has been obtained which indicates epitaxial film quality as good as bulk material.
- Good reproducibility has been demonstrated in the HWE and EDICT processes. As a result, single-crystal HgCdTe films can be grown with predictable thickness and composition.

SECTION 2

TECHNICAL CONSIDERATIONS: DEPOSITION OF SINGLE-CRYSTAL CdTe FILMS

2.1 OBJECTIVE

The objective of this task is the vapor growth of high-purity CdTe epitaxial layers on foreign substrates. The technical approach employed in achieving this goal is the Hot Wall Epitaxy (HWE) method. This method emphasizes the importance of attaining growth conditions as near as possible to thermodynamic equilibrium as well as zero vapor transport losses. Thus, heteroepitaxial CdTe films of high crystalline perfection are expected.

2.2 HOT WALL EPITAXY PROCESS DESCRIPTION

Deposition of single-crystal films of CdTe presents a number of difficulties. First, during evaporation CdTe decomposes into Cd gas and Te_2 gas (unlike the lead chalcogenides which evaporate mainly in molecular form). Second, the vapor pressures of Cd and Te_2 are different by a factor of 20. Third, CdTe is a material which can grow in either the cubic sphalerite or the hexagonal wurtzite structure, depending upon the growth conditions. These structures are similar, but differ in the ordering of their close packed planes. Hence, the tendency of CdTe to form polymorphs and stacking faults during growth is marked.

When CdTe is deposited onto a cold substrate, the result is invariably a fine grain polycrystalline or amorphous film. This situation is not remedied by merely increasing the temperature of the substrate, and a more controlled method is necessary.

In order to overcome these difficulties, the Hot Wall Epitaxy (HWE) method was developed and has been successfully used to grow epitaxial single-crystal films of many materials. The system consists of a heated wall which encloses the source and the substrates in an essentially vapor-tight manner. If the entire source-hotwall-substrate system is held at the same temperature, the system would be at equilibrium and no growth would take place. If, however, a temperature gradient is introduced, the vapor pressure of the system is limited, corresponding to that of the lowest temperature (i.e., that of the substrate). Since the source is at a higher temperature, evaporation of source material takes place and deposition of CdTe on the substrate occurs. The deposition rate depends on the temperature difference between the source and the substrate. The problem is to find a temperature difference which gives a growth rate which is fast enough to be useful and which is slow enough to give good single-crystal epitaxial films.

This method achieves the following ends:

1. It avoids the loss of the high vapor pressure component.
2. It allows growth to occur at a controlled rate close to equilibrium.

2.3 VACUUM SYSTEMS FOR HWE DEPOSITION OF CdTe

The vacuum system is shown in Figure 2-1. It consists of a 400 Welch Turbomolecular (TM) pump backed by a Welch mechanical pump. The bell jar is glass and is 12" in diameter and 18" high. The bell jar has a re-entrant top which is filled with liquid nitrogen when the system is pumped out to improve the vacuum by pumping condensable vapors. The bell jar is connected to the TM pump by means of a stainless steel collar with eight conflat flanges. Three flanges are used for high current leads for the enclosed furnaces. One has provision for four thermocouples. One has a rotary magnetic feedthrough. One is used to attach an ionization gage, and one is used as the system vent through which dry nitrogen may be admitted to break the vacuum. The system is essentially oil-free, is capable of being pumped to 10^{-8} torr, and can be rapidly cycled so that several films can be deposited in one day.

2.4 HOT WALL EPITAXY FURNACE

The Hot Wall Epitaxial furnace has progressed through a number of design changes during the course of the year. Figure 2-2 shows the presently preferred modification, which has produced single-crystal cadmium telluride films on mica and quartz substrates reproducibly. The source consists of a silica furnace tube on which are wound two molybdenum heaters side by side, one to heat the substrate and the other to heat the source and the entire chamber wall. The temperatures of the source and substrate are measured by means of thermocouples. The deposition chamber is contained in the furnace tube and is of the "quasi-closed" type. It consists of a silica source container, a silica baffle, a silica separating cylinder and the substrate. These parts are held together by gravity to form a quasi-closed volume which ensures that there is minimal loss of material and that the vapor pressure of CdTe is close to the equilibrium state when the source and substrate furnaces are adjusted to their optimum temperatures. The initial version of the quasi-closed evaporation source had a thin slot in it, so that a shutter could be inserted to prevent deposition of CdTe onto the substrate until the source and substrate temperatures had been stabilized at the desired values. It is not possible to obtain single-crystal CdTe films wth this earlier evaporation source. Subsequent

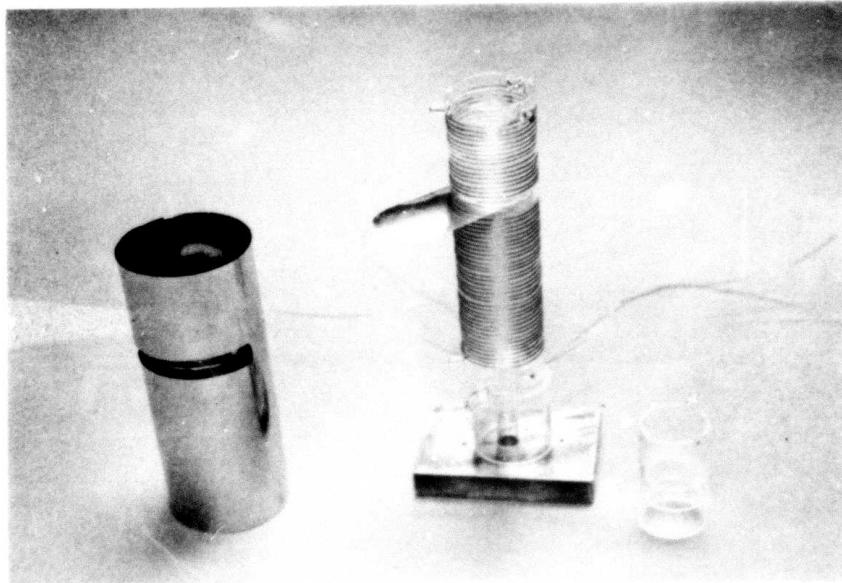
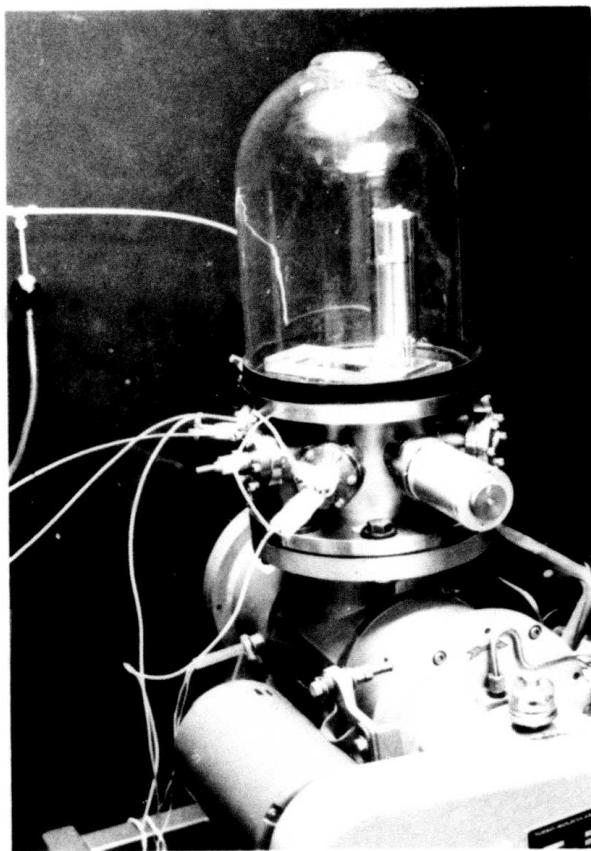


FIGURE 2-1. THE VACUUM SYSTEM FOR HOT WALL EPITAXY DEPOSITION OF CdTe FILMS (TOP) AND INITIAL FURNACE (BOTTOM)

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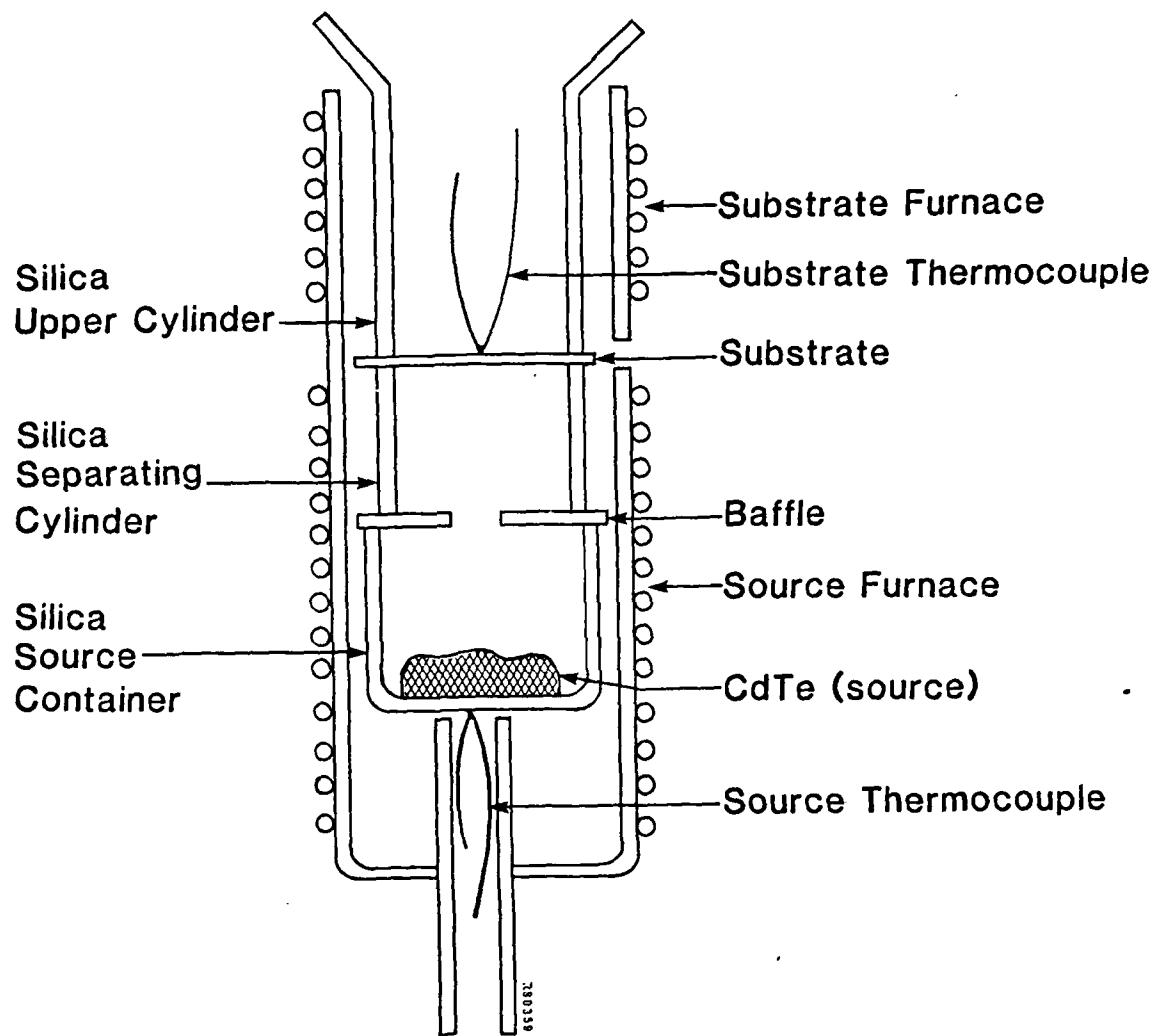


FIGURE 2-2. HOT WALL FURNACE WITH ENCLOSED SOURCE FOR EVAPORATION OF CdTe

experiments determined that it is necessary to have the evaporation source as nearly as possible tightly closed in order to obtain epitaxial films. The reason for this is probably that CdTe decomposes incongruently to Cd and Te_2 at 500°C and the vapor pressures of the component gases are different by more than a factor of 20. It is thus necessary to keep the system as close as possible to thermodynamic equilibrium, and this is done by using the system shown in Figure 2-2.

2.5 HETEROEPITAXIAL GROWTH OF CdTe ON MICA

A series of calibration experiments was performed to determine the range of substrate and source temperature which give single-crystal films of CdTe. These temperatures were measured by two thermocouples placed as close as possible to the source and substrate. There is an unknown but constant difference between the measured and the actual temperature, both in the source and the substrate, due to the fact that the thermocouples are not in physical contact with the source or the surface of the substrate that received the CdTe film. It was impractical to place them in contact with the source material and the substrate surface without running the risk of contamination. The deviations, however, are constant from run to run.

Since the system does not allow the determination of the deposition time by means of a shutter for the reason mentioned in Section 2.3, it is not possible to determine the temperature at which the film commences to nucleate on the substrate.

Table 2-1 shows the reproducibility of thickness of 16 CdTe films. Films #124 through #139 were consecutive depositions. The average film thickness was 2.18 microns with a standard deviation of 0.29 micron. This demonstrates that the Hot Wall Epitaxy apparatus has excellent film thickness control.

The film thickness is independent of the amount of CdTe source material in the boat, and the thickness is also independent upon whether the CdTe in the boat has been used several times or is a fresh charge. It thus appears that the conditions of deposition are close to equilibrium, with the vapor pressure of Cd and Te_2 being determined by the lowest temperature surface inside the quasi-closed Hot Wall Chamber (i.e., the substrate surface).

The time-temperature cycle indicated in Figure 2-3 is suitable to produce single-crystal films of CdTe on mica. The envelope of suitable substrate and source temperatures to give single-crystal films of CdTe on mica is shown in Figure 2-4.

TABLE 2-1. UNIFORMITY OF CdTe FILM THICKNESS

FILM #	SUBSTRATE	FILM THICKNESS (Microns)
124	Mica	2.02
125	Mica	2.09
126	Mica	2.43
127	Mica	3.00
128	Mica	1.80
129	Mica	1.56
130	Mica	1.99
131	Mica	1.69
132	Mica	2.27
133	Mica	2.32
134	Mica	2.04
135	Mica	2.79
136	Mica	1.94
137	Mica	2.30
138	Sapphire	1.87
139	Sapphire	2.00

Mean Thickness - 2.18 microns

Standard Deviation - 0.29 micron

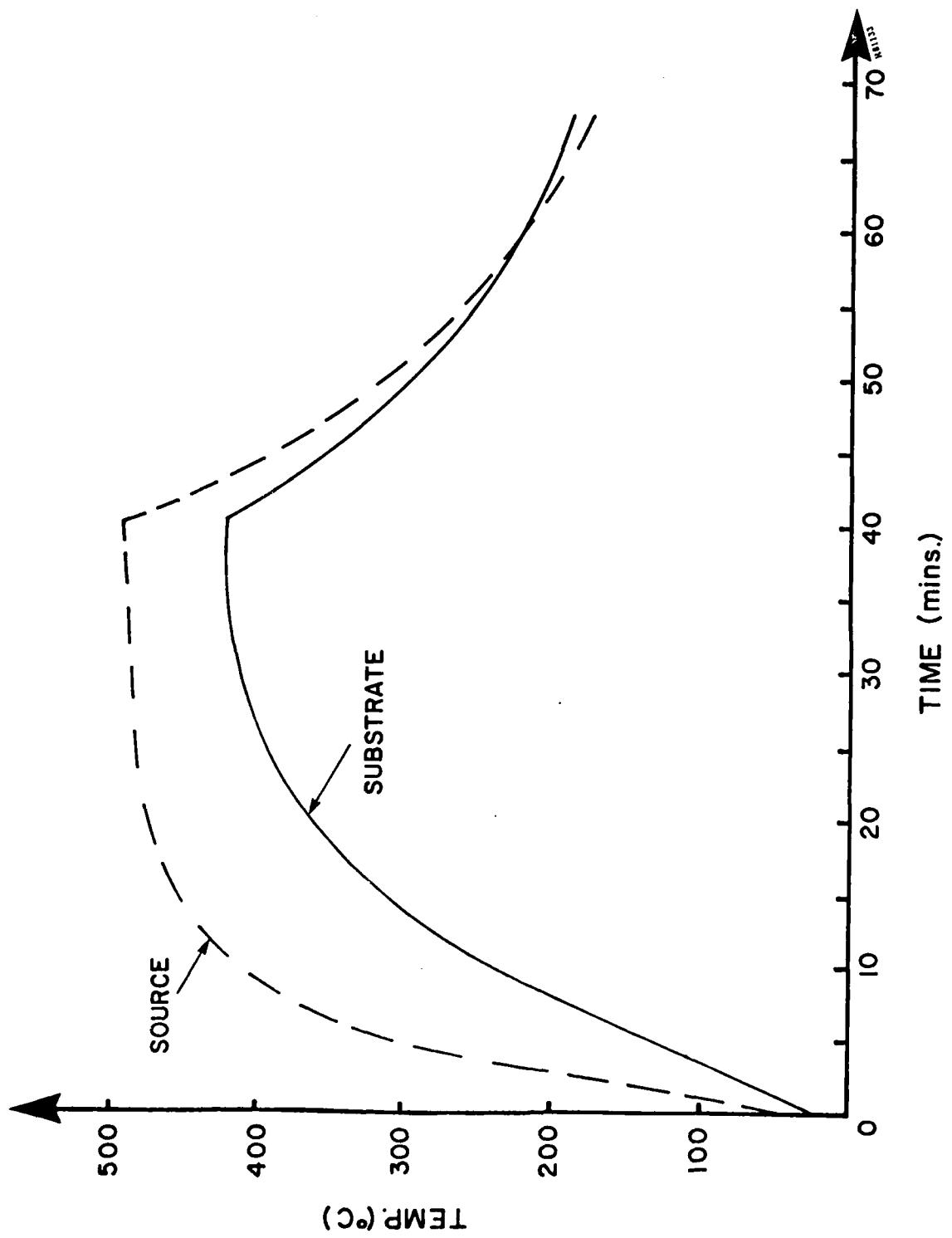


FIGURE 2-3. TIME-TEMPERATURE CYCLES OF THE SOURCE AND SUBSTRATE

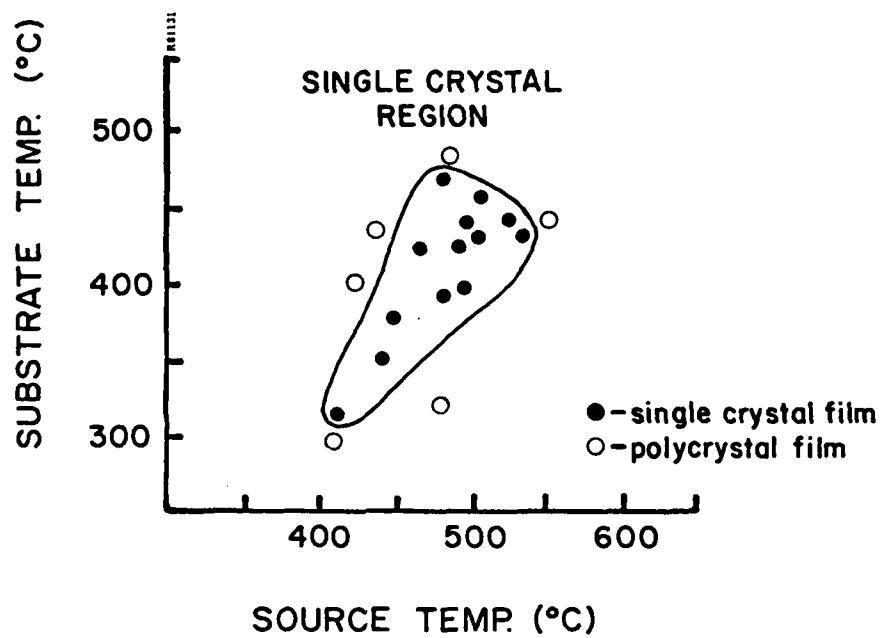


FIGURE 2-4. SOURCE AND SUBSTRATE TEMPERATURE NECESSARY TO GIVE SINGLE CRYSTAL CdTe FILMS ON MICA

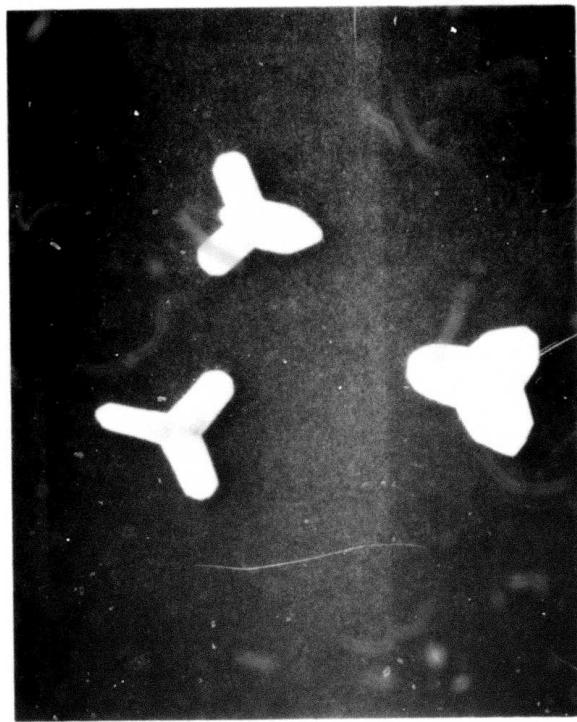
2.6 CHARACTERIZATION OF CdTe FILMS ON MICA

The single-crystal character of the films deposited on mica can be readily observed by an optical microscope under 400x magnification. The surface of the layer shows a structure of pyramids which are aligned over the entire area of the 2.5 cm O.D. substrate. The typical dimension of these pyramids is about 10 microns. This pattern suggests that the (111) plane of cubic CdTe is deposited parallel to the mica face.

If the deposition of the film is arrested at a very early stage, the initial nuclei of the growing film can be seen. Figure 2-5 shows a SEM picture of CdTe nuclei at a magnification of 10,000x. This figure shows that the nuclei are aligned, but that some of them are rotated by 180° with respect to the others. This twin orientation is to be expected because the surface of the mica has a sixfold symmetry whereas the (111) plane of sphalerite has a threefold symmetry. This gives a 180° twinning around the (111) axis which is very common in CdTe single crystals. Figure 2-6 is a SEM photograph of a 5 micron film of CdTe on mica and shows the typical surface of these films at a magnification of 1250x.

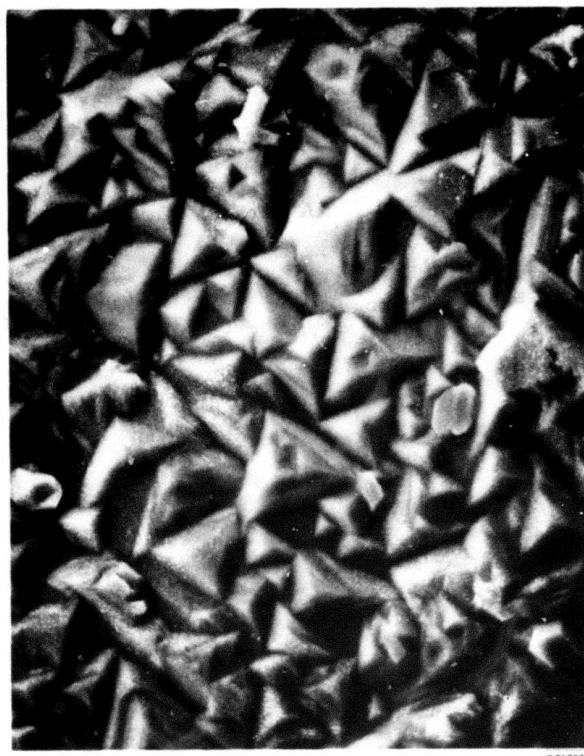
The occurrence of heteroepitaxy, which was suggested by the surface morphology of the as-grown films, was substantiated by x-ray diffraction. Back-reflection Laue patterns were obtained from three widely separated locations on a CdTe film 2.5 cm across and 17.8 microns thick on muscovite mica (specimen M81), viz., from the center and from the periphery at either end of a diameter. In addition, the pattern from the mica substrate was recorded from the opposite face of the specimen, to permit the unequivocal identification of mica contributions to the film pattern. The three CdTe patterns were identical, indicating the absence of mutual misorientation within the sensitivity of the technique. It was concluded that the region spanned by the sampled areas is a single crystal. Additional patterns from this and other CdTe/mica specimens confirmed the single-crystal nature of the films.

The macroscopic appearance of the films suggests that each is comprised of several large subgrains, perhaps induced by substrate flexure during deposition. Back-reflection Laue patterns with the x-ray beam straddling apparent subgrain boundaries failed to reveal fragmentation in all but one case, where a double pattern with a mutual misorientation less than or equal to 2° was observed.



1 μ m

FIGURE 2-5. SEM PHOTOMICROGRAPH SHOWING CdTe NUCLEI
(10,000x Magnification)



10 μ m

FIGURE 2-6. CdTe FILM (5 MICRONS THICK) DEPOSITED ON MICA

A typical back-reflection Laue pattern from the CdTe film of specimen M81 is presented in Figure 2-7. It shows a high degree of symmetry and is readily interpreted to reveal the following orientation relationship:

(111) CdTe/(001) muscovite

i.e., the close-packed double layer of CdTe, which is polar and has trigonal symmetry, is parallel to the unique $(\text{Si}_3\text{Al})\text{O}_{10}$ hexagonal net of the mica. This is the heteroepitaxial relationship predicted on general grounds and observed previously.⁽¹⁾ The patterns were indexed according to cubic-system symmetry, since Debye-Scherrer analysis of as-deposited films had shown them to have the sphalerite structure of the cubic polymorph rather than the wurtzite structure of the hexagonal polymorph.

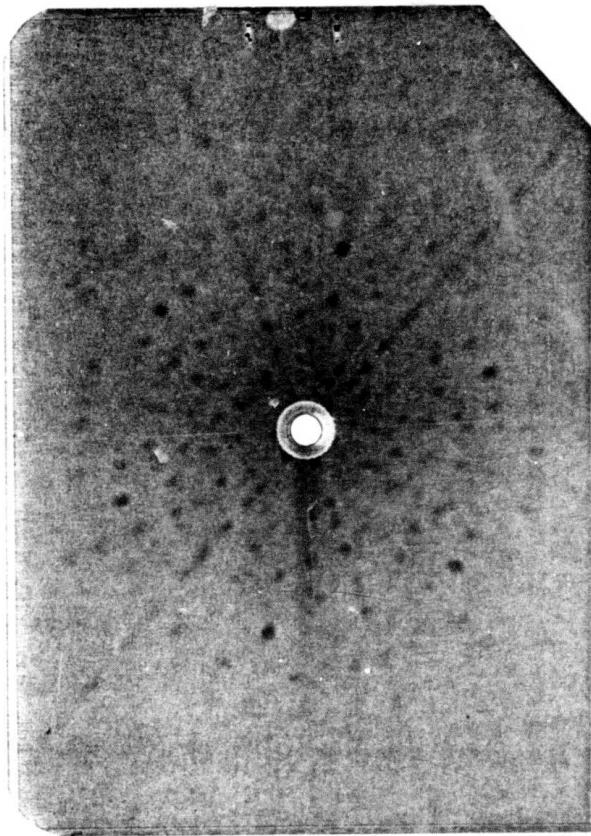
Nevertheless, the CdTe patterns exhibit excess symmetry for a cubic crystal, being sixfold rather than threefold. This is interpreted as evidence that the films are twinned, a result which is to be expected because of the high degree of pseudosymmetry inherent in the sphalerite structure. As shown in Figure 2-7, the patterns are consistent with the sphalerite twinning operation: 180° rotation about the normal to (111).

The results of the back-reflection Laue analysis were further corroborated by the diffractometer method used in the reflection geometry. The following observations were made:

- The diffraction patterns from various regions of the same CdTe/mica specimen match, indicating that the film is a single crystal.
- The diffraction peaks comprising the patterns have the relative intensities and angular positions to be expected for a CdTe single crystal of cubic symmetry.
- Rotation of the specimen in its own plane causes all diffraction peaks except (111) to pass through intensity minima (detuning), indicating that the film is a single crystal with (111) parallel to the substrate surface.

2.7 FILMS DEPOSITED ON OTHER SUBSTRATES

We have deposited films of CdTe onto single-crystal quartz and single-crystal sapphire, both cut perpendicular to the hexagonal c axis. Laue x-ray photographs showed that the polished face of the sapphire crystals were misaligned from the normal to the c axis by $8^\circ \pm 1^\circ$. The crystal quartz was misaligned by $1^\circ \pm 1^\circ$.



(a)

FIGURE 2-7. BACK REFLECTION LAUE PATTERN FROM CdTe FILM ON MUSCOVITE MICA (SPECIMEN M81). (a) Pattern as recorded, negative image; molybdenum radiation, 20 kV/20 mA, 5 h exposure, (b) Important zone hyperbolae of the pattern, showing the 6-fold pseudosymmetry of the twinned crystal. (c) and (d) Components of the pattern, showing the 3-fold symmetry of the untwinned crystal in (111) orientation, with the prominent diffraction maxima indexed; the two components are related by the twinning operation: 180° rotation about the normal to (111).

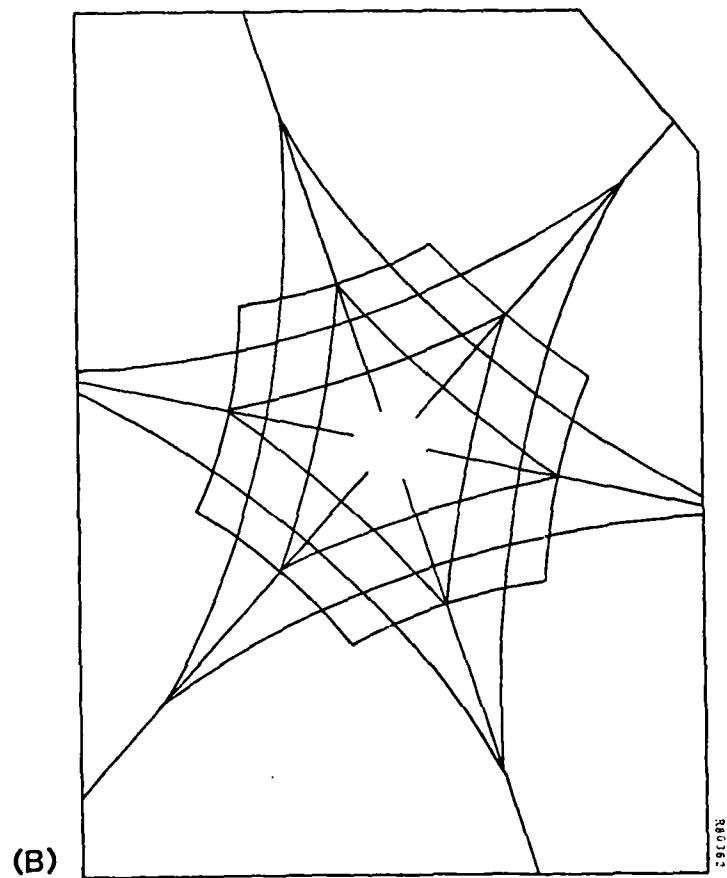


FIGURE 2-7. BACK REFLECTION LAUE PATTERN FROM CdTe FILM ON MUSCOVITE MICA (SPECIMEN M81) (Continued)

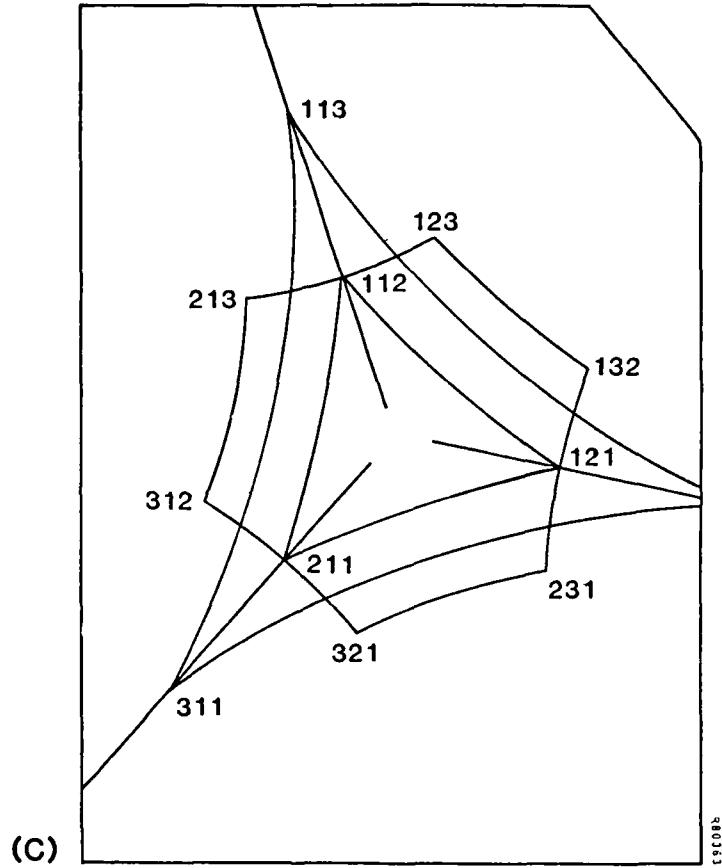


FIGURE 2-7. BACK REFLECTION LAUE PATTERN FROM CdTe FILM ON MUSCOVITE MICA (SPECIMEN M81) (Continued)

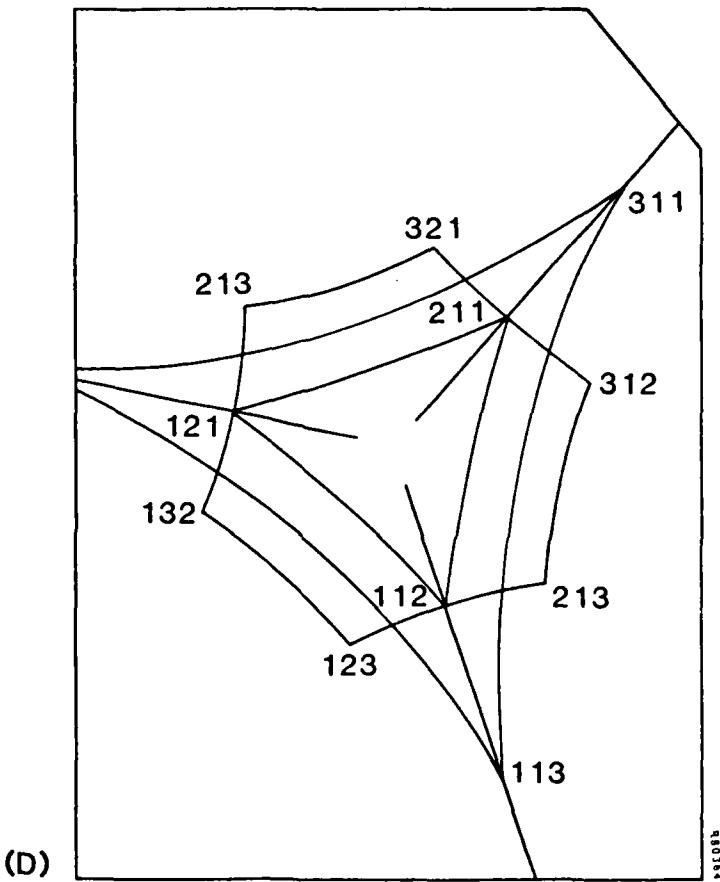


FIGURE 2-7. BACK REFLECTION LAUE PATTERN FROM CdTe FILM ON MUSCOVITE MICA (SPECIMEN M81) (Concluded)

CdTe films were deposited on these substrates using the HWE method. Initially, polycrystalline films were obtained on both substrates when the deposition parameters were held the same as for the successful films on mica. X-ray patterns of these films showed many small crystals for the films on quartz and generally "powder pattern" rings for the films on sapphire. There were two possible reasons why the films did not deposit as single crystal: inadequate cleaning procedures or the misorientation of the substrate. By comparison, the mica substrates, being cleaved, were perfectly oriented and were automatically clean without any chemical treatment.

The standard cleaning method for nonmica substrates was to use a solvent such as acetone for organic materials, followed by a deionized water treatment and then an acid cleaning, such as with aqua regia, followed by extensive rinsing in deionized water. An alternate cleaning method was attempted with crystalline quartz, which was to immerse the quartz for 20 seconds in 20% hydrofluoric acid after normal acetone treatment, to etch away 100 nm of the surface. The acid was then diluted in a running stream of deionized water until all traces of acid had gone. The substrate was taken to the vacuum system still immersed in deionized water and was taken out and blown dry by means of a nitrogen jet immediately before being placed in the vacuum system.

The result of deposition on this substrate was a single-crystal film of CdTe as determined by microscopic examination and as confirmed by x-ray technique. The adherence of the single-crystal film of CdTe to the quartz substrate was very poor, and the film fell off after an x-ray picture had been taken. It was assumed that this was the result of poor thermal expansion coefficient match. Perpendicular to the c-axis the thermal expansion coefficient of quartz is $13 \times 10^{-6}/^{\circ}\text{C}$, whereas that for CdTe is a $5 \times 10^{-6}/^{\circ}\text{C}$. The thermal expansion coefficient of sapphire perpendicular to the c-axis is $5.5 \times 10^{-6}/^{\circ}\text{C}$, and thus the match with CdTe and HgCdTe is very good. In fact, sapphire has been used as substrate material for the fabrication of HgCdTe photoconductive arrays for over a decade.

Since single-crystal CdTe was obtained on quartz as a result of removing a surface layer of the quartz substrate and keeping the substrate immersed in dionized water up to the time of deposition, it was therefore decided to try the same procedure for the sapphire substrate. However, sapphire is not soluble in HF, so a hot solution of phosphoric acid was used to remove the surface layer instead. After treatment, the sapphire substrate was wetted by water, whereas before treatment with phosphoric acid, water beaded on the substrate surface. After the removal of the substrate surface, the

sapphire disc was kept under deionized water until just before its use in the vacuum system. The CdTe film deposited on this substrate was polycrystalline. It thus appears that both the cleaning procedure and the exactness of the substrate orientation are of prime importance to the crystallinity of the deposited CdTe film.

CdTe films were also deposited onto silicon substrates earlier in the program, but this was before the optimized form of evaporation source had been made; thus these films were polycrystalline. There was not sufficient time to return to deposition of CdTe films on silicon after the improvement of the deposition method.

SECTION 3

TECHNICAL CONSIDERATIONS: VAPOR EXCHANGE OF CdTe TO FORM HgCdTe

3.1 OBJECTIVE

The objective of this task is the vapor growth of uniform HgCdTe epitaxial layers from the previously deposited CdTe heteroepitaxial films. The technical approach employed is the Evaporation Diffusion at Constant Temperature (EDICT) method. This method closely resembles the Hot Wall Epitaxy (HWE) technique in that isothermal conditions for the source, ampoule wall, and substrate are emphasized and thus true thermodynamic equilibrium is assured. The only difference between the HWE and the EDICT method is that in addition to sublimation and condensation, the EDICT process utilizes a third growth mechanism, which is diffusion in the solid phase. Impinging HgTe first accumulates at the CdTe film surface and then diffuses into the CdTe layer while CdTe diffuses up to the surface until equilibrium is reached. Since the entire process, i.e., both vapor and solid phase exchange, takes place close to thermodynamic equilibrium, excellent HgCdTe epitaxial films of uniform composition and perfect crystalline quality are thus expected.

3.2 EDICT PROCESS DESCRIPTION

To change a film of CdTe into a film of HgCdTe, it is necessary to diffuse Hg and Te into it. The diffusion of the correct amount of mercury gives the correct x value, and the diffusion of the correct amount of tellurium determines the stoichiometry of the film.

As an example, to convert 1 gm of CdTe to $Hg_{(1-x)}Cd_xTe$ with an x value of 0.2, it is necessary to diffuse 5.5 grams of HgTe into it, and as a result, the volume increases by a factor of 4.15. Thus, there must be a considerable amount of atomic movement to achieve the required result.

The early work on the EDICT method was done on bulk samples at the C.N.R.S. Laboratory in Paris.⁽²⁾ A slab of CdTe and a slab of HgTe would be enclosed in a sealed, evacuated quartz ampoule. After a number of days at isothermal conditions at temperatures in the range 450 to 650°C, some of the HgTe would be transferred to the CdTe slab, but no evidence of reverse transfer of CdTe to the HgTe slab would be found. Examination of the CdTe slab showed that the growth layer at the surface would have a strong gradient of x value normal to the surface, and the layer would remain essentially with x = 1 at the interface and x = 0 at the surface. This growth was found to depend

upon the temperature, time of soaking, the distance apart of the slabs of material, and the pressure of mercury. This last parameter could be separately adjusted by placing excess mercury in the ampoule.

The results obtained by the bulk EDICT process were interesting but lacking in practical use because of the steep gradient in x normal to the substrate surface. This difficulty was overcome by the group at the Warsaw Technical Academy, who had the simple but brilliant idea of performing similar experiments with CdTe in thin-film form. Under these conditions, the growing layer would reach the CdTe-substrate interface, and no further supply of CdTe would be available. If the supply of HgTe was also limited, the x value of the film would become uniform with depth. It was found that, if the HgTe supply was correctly calculated, all the HgTe would diffuse into the CdTe film, which would end by having the x value which had previously been calculated from the initial weights of CdTe and HgTe in the ampoule. (The excess weight of Hg in the ampoule does not affect the x value of the film, for it remains in the ampoule.) The measured x value uniformity of these films is excellent both parallel and normal to the surface.

The steps by which this process occurs are believed to be as follows:

1. As the temperature rises in the ampoule, the mercury, and tellurium pressures also rise. The vapor in the ampoule is almost all mercury, and the surface of the CdTe is covered by an equilibrium layer of mercury until the surface reaches the stoichiometry limit. At this point, no more mercury can be absorbed onto the surface.
2. The flux of Te_2 onto the growing surface is very much less than that of Hg, and the Te_2 molecules are readily captured on the Hg rich surface to cause HgTe to be formed. Note there would be no similar capturing phenomenon of Cd on the HgTe surface because that surface would already be metal saturated.
3. The final formation of the film takes place by in-diffusion of Hg and out-diffusion of Cd until all the HgTe has been used up and the film has been homogenized. At this point there is no further driving force and the system reaches equilibrium.

3.3 EDICT AMPOULES AND FURNACE

The ampoule configuration used in the vapor transport/solid exchange growth of single-crystal HgCdTe films is shown in Figure 3-1. The ampoule consists basically of two telescoping silica tubes which are closed at one end. The I.D. of the outer tube is

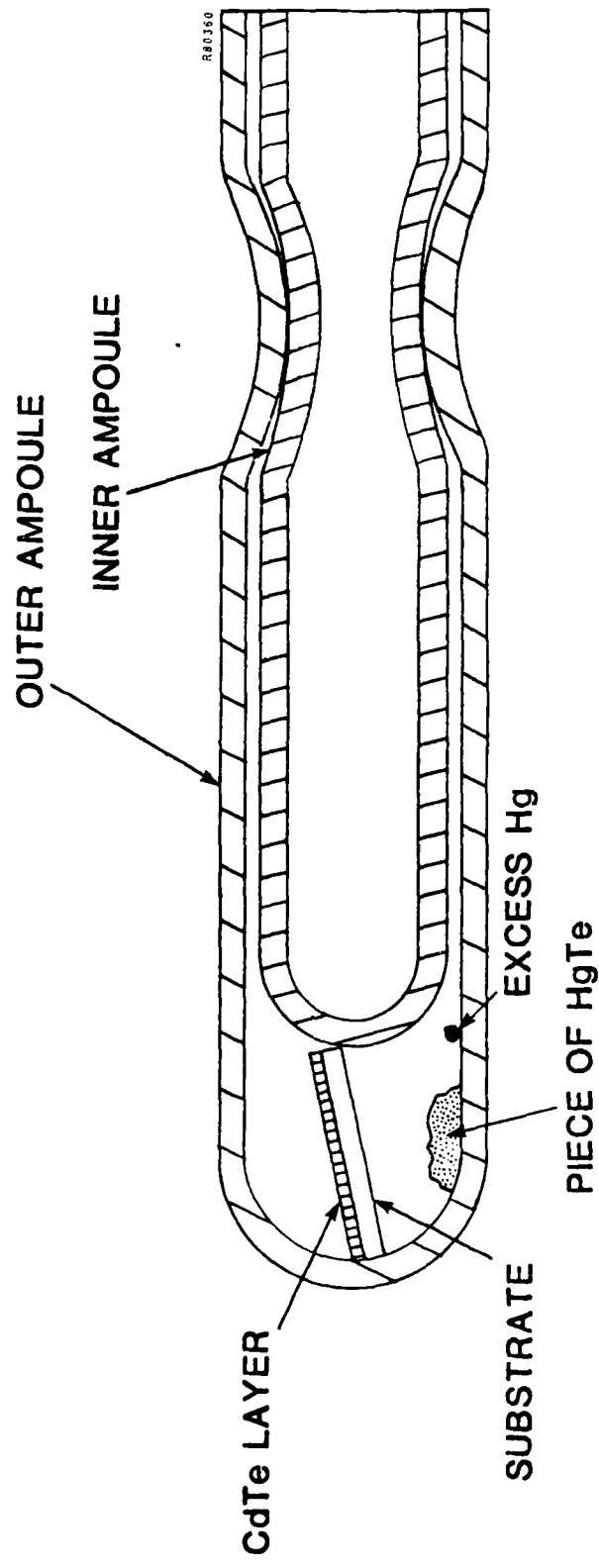


FIGURE 3-1. SCHEMATIC OF VAPOR EXCHANGE APPARATUS (AT NERC)

large enough that a 1/2" square substrate can be accommodated. The ampoules are thoroughly cleaned and then assembled with the CdTe film, a piece of HgTe and a small amount of excess Hg. The weight of HgTe is calculated so that the desired x value of HgCdTe is achieved after complete vapor transport to and diffusion into the CdTe films have occurred. The weight of Hg is chosen so that at the growth temperature, a predetermined pressure of Hg exists in the ampoule. When the free volume of the ampoule has been adjusted by sliding the inner silica tube to its correct position, the ampoule is evacuated to 10^{-6} torr on the same vacuum system that is used to deposit the CdTe films, and the two tubes are fused together as shown in Figure 3-1.

The ampoule is placed in a furnace at room temperature, and the furnace temperature is then slowly raised to the desired temperature. The temperature of the furnace is maintained uniform throughout the entire ampoule length by placing a sodium heat pipe inside the furnace as shown in Figure 3-2. The entire growth process typically takes several days. If desired, the as-grown sample can be annealed at a lower temperature to adjust stoichiometry defect concentrations in the same ampoule without breaking the vacuum.

3.4 EDICT EXPERIMENTS

A number of specimens of CdTe films on mica were subjected to vapor phase transport by the EDICT technique. The parameters of growth (i.e., EDICT time, EDICT temperature, anneal time, anneal temperature, Hg pressure, and final film thickness) together with the intended and actual x value of the final HgCdTe films are given in Table 3-1 for 14 samples.

The ampoules used for growth were cleaned by the standard quartz cleaning method, and then the films and the additional HgTe and Hg were loaded. The films on mica were cut into 1.2 cm x 2 cm rectangles to fit inside the vapor ampoules. The weight of the films was known, so the weight of HgTe to be added was readily calculated. The weight of free Hg to be added was calculated from the free volume of the ampoule and the EDICT temperature to be used, knowing the required Hg pressure for the experiment.

The ampoules were pumped to a pressure of 10^{-6} torr and then sealed off. After the EDICT and annealing treatment had been carried out, the ampoules were cooled to room temperature and opened, and the weight of the substrate and film combined was again measured so that the weight of the HgTe could be determined. The amount of HgTe transferred to the film could be calculated and the x value of the $Hg_{(1-x)}Cd_xTe$ determined.

FURNACE CAVITY

EVACUATED
QUARTZ
AMPOULE

CdTe
FILM

HEAT PIPE

HgTe
Hg

T_C

601134

FIGURE 3-2. A HEAT PIPE IS PLACED INSIDE THE EDICT FURNACE TO ENSURE GROWTH IN THERMODYNAMIC EQUILIBRIUM

TABLE 3-1. SUMMARY OF 14 HgCdTe SAMPLES GROWN BY THE EDICT METHOD

SAMPLE #	EDICT TIME (HR)	EDICT TEMP (°C)	ANNEAL TIME (HR)	ANNEAL TEMP (°C)	Hg PRESSURE (ATMOSPHERE)	FINAL FILM THICKNESS (μm)	INTENDED X VALUE	ACHIEVED X VALUE
M82	96	500	16	300	4.8	7.7	0.2	0.85
M99	96	500	-	-	0.5	32.5	0.2	0.2
M106	96	500	-	-	0.25	30.0	0.2	0.2
M107	120	475	164	250	0.5	64.0	0.2	0.24
M124	120	475	164	250	0.25	10.6	0.2	0.2
M126	96	475	216	250	0.125	13.0	0.2	0.2
M132	96	475	216	250	0.25	12.4	0.2	0.19
M133	96	475	216	250	0.50	7.0	0.2	0.34
M128	96	525	-	-	0.75	2.3	0.2	0.85
M130	144	525	-	-	1.0	2.8	0.19	0.75
M100	120	500	-	-	0.5	11.1	0.2	0.26
M135	480	500	-	-	0.5	15.4	0.2	0.2
M127	480	500	-	-	0.5	9.3	0.2	0.33

The effect of excess Hg vapor pressure on the conversion of these films can be seen from Table 3-1. In cases where the excess Hg pressure was greater than 0.5 atmosphere, growth did not go to completion. (See samples M82, M128 and M130.) Five films for which the excess Hg pressure was 0.5 atmosphere (M107, M125, M133, M100, M127) were close to but did not achieve the intended x value, and two films for which the excess Hg pressure was 0.5 atmosphere (M99 and M135) reached the designated x value of 0.2 within experimental error. The four films for which the excess Hg pressure was less than 0.5 atmosphere (M124, M126, M106 and M132) all attained the designated value of x within experimental error, even though two of the films were treated at the lowest temperature (475°C) and for the shortest time (96h) used in the EDICT experiments. The upper limit of excess Hg pressure has thus been determined to be 0.5 atmosphere. The lower limit of excess Hg pressure has not yet been determined. In fact, good EDICT results have been achieved in bulk CdTe by Gatos⁽³⁾ by using an excess of Te instead of an excess of Hg. In this case, the subsequent annealing of the films to n-type would have to be performed in a separate ampoule.

3.5 CHARACTERIZATION OF HgCdTe FILMS

Film characterization included composition and its uniformity, crystalline perfection and electrical properties. The results are presented in this section.

The alloy composition of the HgCdTe layer can be determined by means of either transmittance or reflectance spectrometry. The leading edge of either the spectral transmittance or reflectance corresponds to the fundamental absorption edge of the material under study. The transmission technique, in the case of using mica as the substrate, is not applicable because mica is opaque in the infrared. As a result, reflectance measurements of HgCdTe films on mica substrates were made. One typical spectral reflectance of HgCdTe film grown on mica substrate is shown in Figure 3-3. Also in the figure is the reflectance from a bare mica substrate for reference purposes. The angle of incidence of this measurement was 45° , and the area of the film illuminated was about 1 cm^2 . The sudden change in reflectance at $8\text{ }\mu\text{m}$ is caused by the abrupt drop in absorption coefficient of the film, indicating fundamental absorption. The fact that the rise in reflectance with wavelength is rapid indicates that the film is very uniform in composition over an area of 1 cm^2 as well as normal to the surface of the layer. The fact that the reflectance change is at $8\text{ }\mu\text{m}$ at room temperature is indicative of a composition of $\text{Hg}_{(1-x)}\text{Cd}_x\text{Te}$ for which $x = 0.2$, which agrees with the value calculated by the change of weight of the film during the EDICT process.

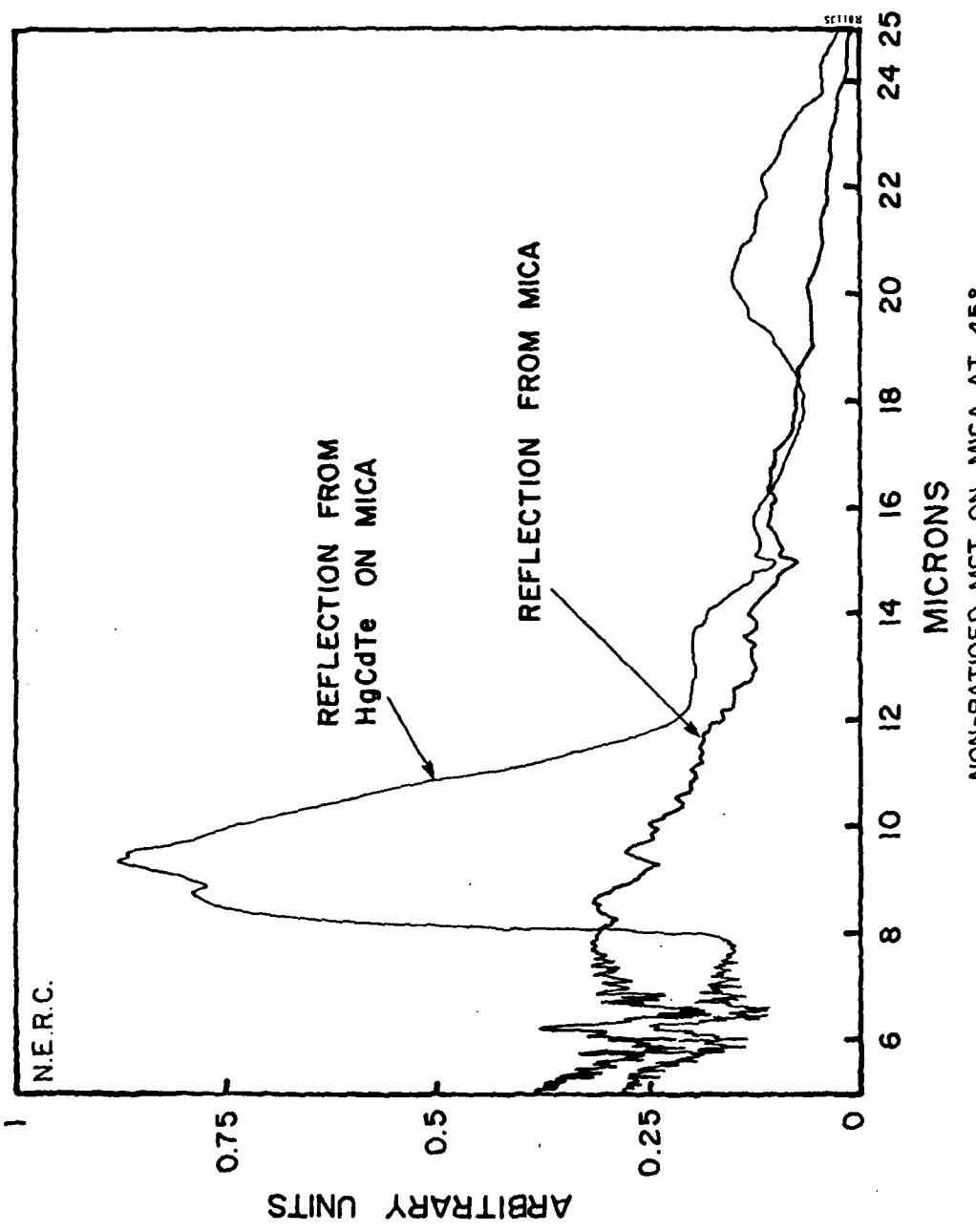


FIGURE 3-3. FOURIER TRANSFORM REFLECTANCE SPECTROSCOPY MEASUREMENTS TAKEN ON A HgCdTe/MICA SAMPLE AND A BARE MICA SUBSTRATE

To evaluate the compositional uniformity across the surface of the HgCdTe films, electron beam microprobe analysis was first employed. Although this technique offers excellent spatial resolution, it has a rather poor resolution in determining the mole fraction variation in HgCdTe. Our calibration study indicated that the precision of the electron beam microprobe technique is good to ± 0.01 in alloy composition. Thus, other evaluation techniques with better sensitivity have to be used.

The most accurate technique for measuring compositional uniformity is the spectral cutoff of electro-optical devices fabricated evenly across the film surface, because the spectral response of an infrared sensing device such as a photoconductor or a photovoltaic detector is a direct measurement of the bandgap of the material. For this reason, p-n junctions were formed by impurity diffusion through a mask pattern, so that a number of samples were evenly distributed across the entire HgCdTe film surface. Leads were then attached to both sides of the junction, and relative spectral responses were measured at 77°K . The composition and its uniformity can then be determined from the well-established bandgap-composition relationship. One should emphasize that the aim for these test structures is to measure compositional uniformity across the surface of the films rather than to evaluate the device quality of the HgCdTe epitaxial material grown by the Hot Wall/EDICT process. The latter is beyond the scope of this program.

Figure 3-4 shows four photovoltaic test structures fabricated across a HgCdTe film of a nominal size of 1.2×1.2 cm. The data showed the average value and variation in cutoff wavelength to be $10 \pm 0.08 \mu\text{m}$, which corresponds to an average composition value x , with variation, of 0.2190 ± 0.00065 . The precision of the Fourier Transform Spectrometer with which these data were taken is about $0.05 \mu\text{m}$, which corresponds to 0.00050 in composition limit. Thus, most of the measured variation was due to equipment uncertainty rather than the material itself. A uniformity in composition of ± 0.00067 is one of the best ever reported in HgCdTe material grown by any method.

Crystalline perfection of the EDICT films was determined by means of back-reflection Laue diffraction. As indicated in Section 2.5, single-crystal CdTe films were obtained by means of Hot Wall Heteroepitaxy. The question remaining was whether the EDICT process would favorably or adversely affect the crystallinity of the final HgCdTe layer.

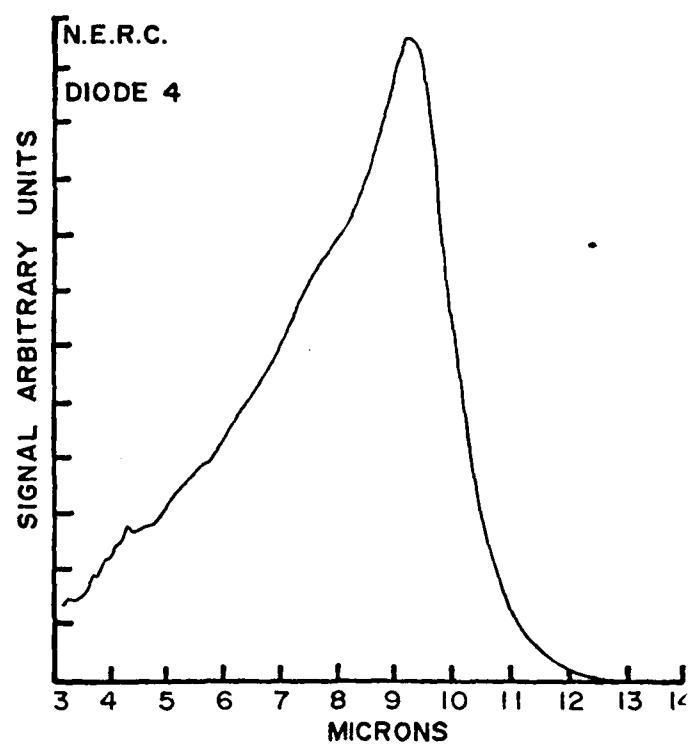
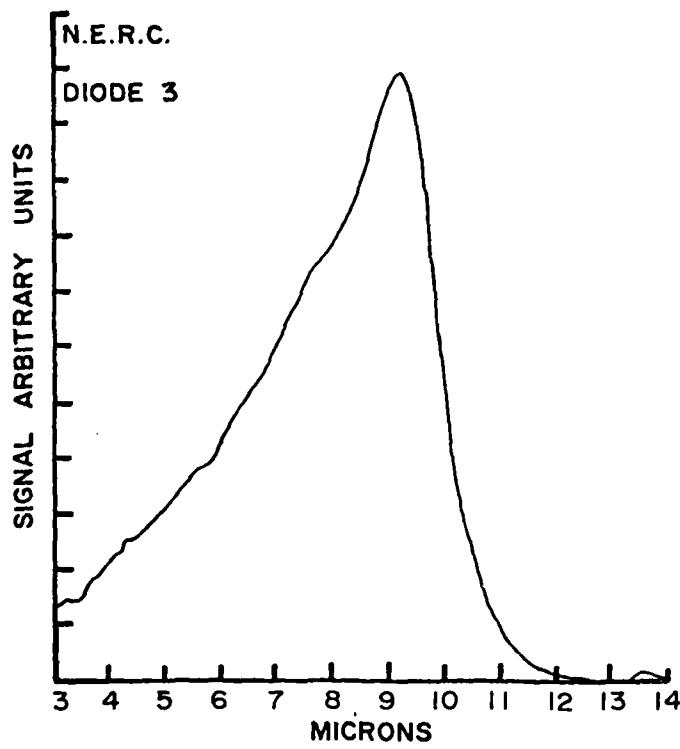
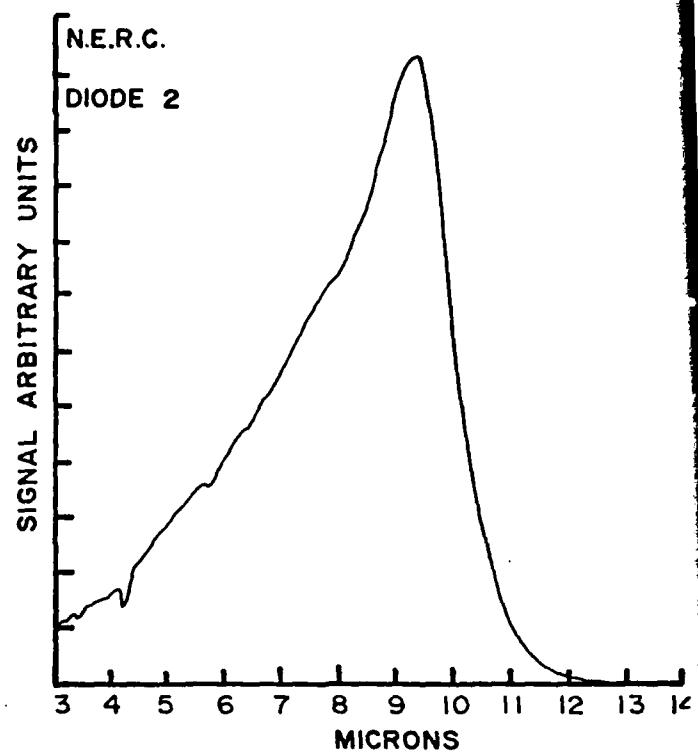
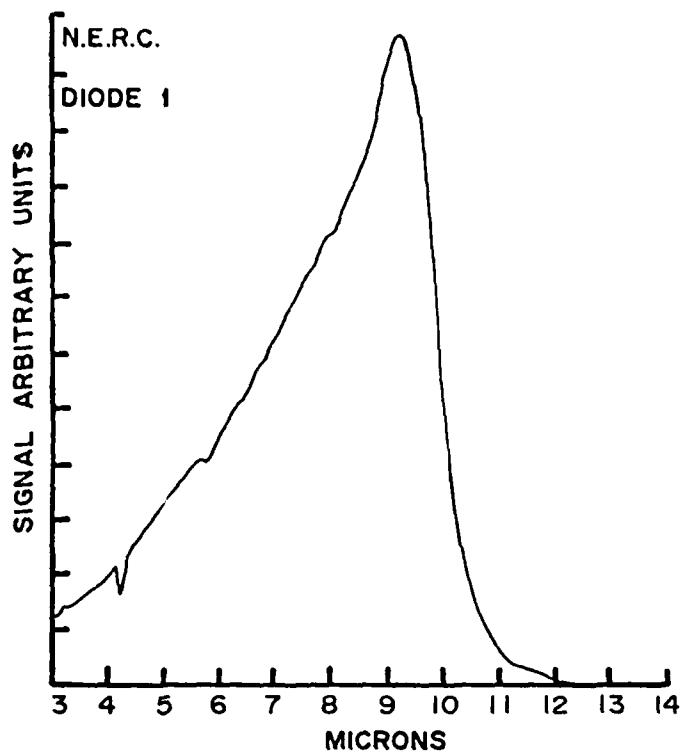


FIGURE 3-4. COMPOSITIONAL UNIFORMITY OF 0.2190 ± 0.00067 ACROSS
A 1.2×1.2 cm AREA MEASURED WITH THE FOURIER
TRANSFORM SPECTROMETER WHICH HAS A PRECISION
LIMIT FOR RESOLVING X OF ± 0.00050

Figures 3-5 (a) and (b) show the improvement in crystalline quality as a result of the EDICT process. The upper photograph is a Laue diffraction pattern of a CdTe film grown on mica by the Hot Wall method. The high degree of symmetry revealed in Figure 3-5 (a) indicates the single-crystal nature of the CdTe film. Comparing Figure 3-5 (a) to (b) which is a Laue back reflection taken from a EDICT film, one finds that the degree of symmetry improves. Specifically, most of the "background" spots clustered along symmetry lines disappear. This is an indication of improved crystalline perfection as a result of the EDICT process.

To illustrate clearly the favorable effects of the EDICT process on crystallographic defects, a bulk CdTe wafer acquired from II-VI, Inc. was studied before and after it was subjected to the EDICT process. A Laue back reflection x-ray was first taken prior to the EDICT process, and the pattern was shown in Figure 3-6 (a). Large dots and their irregular shape and somewhat uneven intensity indicated macroscopic crystal defects and low-angle misorientations. This CdTe wafer was then subjected to the EDICT process, and a relatively thick (4 mils) HgCdTe layer was grown at the surface with a compositional gradient normal to the surface as expected. A Laue pattern was then taken, and the result was shown in Figure 3-6 (b). It was apparent from this photograph that although the diffraction pattern did not change, the size of the dots and the "substructures" inside the dots was drastically reduced. This result together with those in Figure 3-5 demonstrate that the EDICT process greatly improves crystal perfection of the final HgCdTe film.

Electrical characteristics such as mobility and carrier concentration were measured by the Van der Pauw method. The as-grown HgCdTe films were p-type. This was expected because the EDICT process took place at temperatures from 450 to 650°C. The conductivity type of these films could be altered via low temperature annealing. A number of films were annealed at 250°C for three to four days under Hg pressure. Van der Pauw samples were formed by cutting the films into squares of 3 mm size. Contacts were made by wire bonding on the extreme corners of the squares. The contacts were made as small as possible to minimize measurement error. The samples were then mounted between the pole pieces of a Varian magnet which was capable of maintaining a uniform field of 3K gauss. Hall measurements were made at room temperature and at 77°K.

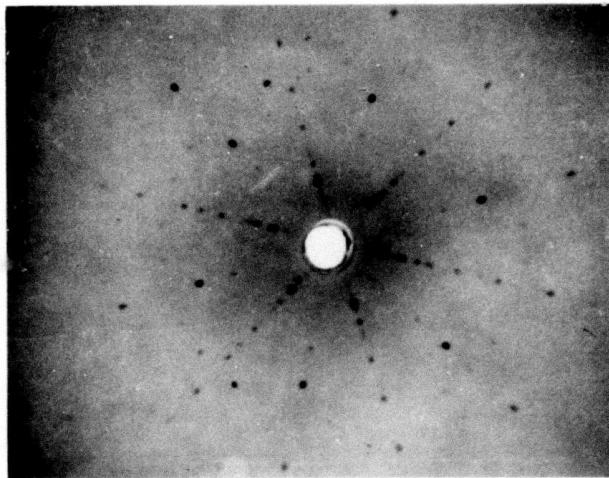


FIGURE 3-5(a). LAUE X-RAY PATTERN OF A SINGLE CRYSTAL CdTe FILM
ON MICA

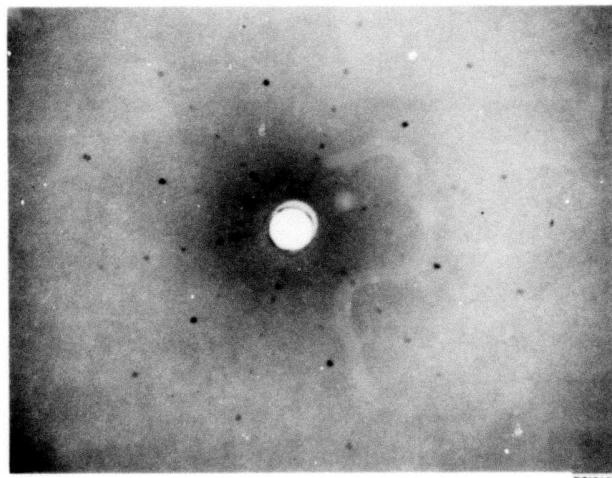


FIGURE 3-5(b). LAUE X-RAY PATTERN OF THE SAME SAMPLE SHOWN ABOVE
AFTER THE EDICT PROCESS SHOWING IMPROVED
CRYSTALLINE QUALITY

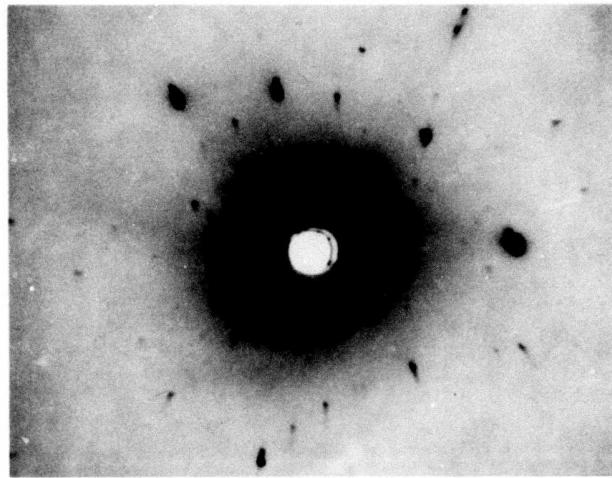


FIGURE 3-6(a). LAUE X-RAY PATTERN TAKEN ON A BULK CdTe WAFER
(1 mm Thick)

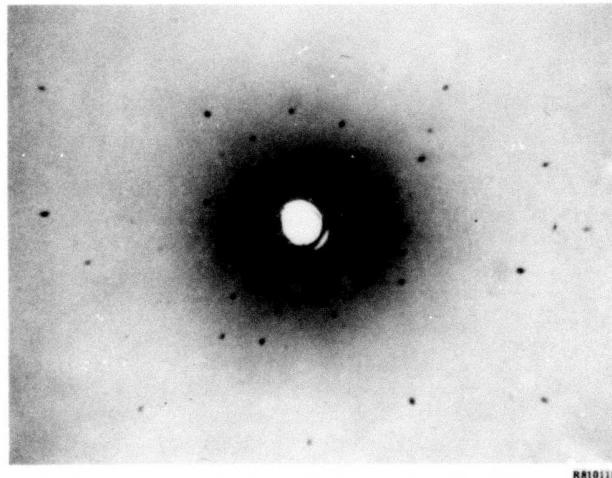


FIGURE 3-6(b) LAUE X-RAY PATTERN TAKEN ON THE SAME SAMPLE
AS (a) BUT AFTER THE EDICT PROCESS

The values of electron concentration in these HgCdTe films ranged from 6 to $20 \times 10^{15} \text{ cm}^{-3}$ while those of mobility ranged from 0.5 to $1.5 \times 10^5 \text{ cm}^2/\text{V-s}$. The carrier concentrations were high compared to good bulk-grown HgCdTe. The electron mobilities, however, were comparable to bulk material, considering the fact that the carrier concentrations were relatively high and impurity scattering would have lowered the mobility.

Historically, materials grown by epitaxy techniques, whether in the liquid or vapor phase, are inferior to those grown by bulk techniques in terms of electrical properties. Mobility has been one of the key parameters for the evaluation of the quality of film grown. A good mobility, meaning it is as high as that of bulk material, indicates that the epitaxial film is of high quality. The high carrier concentrations measured in the EDICT layers are believed to be caused by contamination due to handling rather than inherent in the growth processes. Impurity control will be one of the prime objectives in future development.

SECTION 4

TECHNICAL CONSIDERATIONS: PULSED ELECTRON BEAM SURFACE PROCESSING

4.1 OBJECTIVES

There were two objectives in studying pulsed electron beam processing of CdTe films (deposited by HWE) during this time period. The first was to improve the faceted surface morphology by polishing through melting a thin surface layer. The second objective was to improve the initial crystal structure of the deposited CdTe films through rapid liquid-phase heteroepitaxy. Pulse processing of the film as CdTe was preferred over processing of HgCdTe because of the higher mercury vapor pressure.

4.2 METHOD

The pulsed electron beam apparatus was previously described.⁽⁴⁾ For experiments reported here, the electron beam with the energy spectrum shown in Figure 4-1 was used. The fixed pulsed width was 100 ns. The angle of incidence of electrons upon the sample surface was between 0 and 45°. Total fluence was varied from 0.2 to 0.6 J/cm².

The electron beam is used to melt the surface of the film to a varying depth, up to 4 microns (approximately). As a liquid, surface tension pulls the film flat and reduces the heights of structures, in effect, polishing the surface. Liquid-phase epitaxy upon the unmelted subsurface material restores the crystal structure of the molten region as it cools. The process for thin films is fast enough (less than 10 microseconds) that out-diffusion of Cd from the surface is minimized.

To improve the twinned crystal structure of the HWE CdTe film, the pulsed electron beam was used to melt the entire film to the insulating substrate interface. It is believed that rapid liquid-phase heteroepitaxy would improve the crystal structure, in part because melting would diffuse any contamination at the original interface, in part because very fast growth rates (1 m/s) should favor only one orientation and reduce twinning.

4.3 SURFACE POLISHING

The surface of the CdTe films after HWE is dull and nonreflective, and appears to be highly absorptive. After pulsed electron beam (PEB) irradiation the surface appears to be highly reflective, or polished, with a grey metallic color. Reflection of illuminating light causes this surface to appear dark in Figure 4-2.

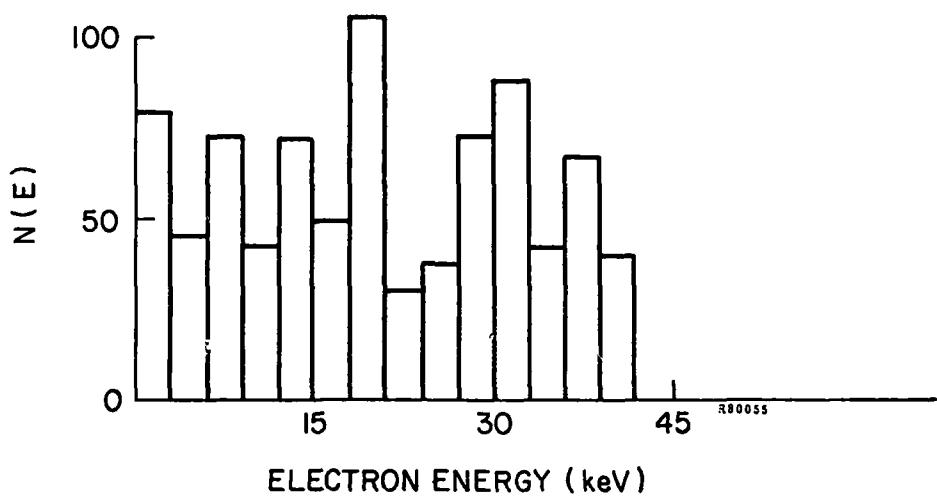


FIGURE 4-1. ELECTRON ENERGY SPECTRUM OF BEAM USED TO PROCESS CdTe



FIGURE 4-2. HWE DEPOSITED CdTe FILM ON MICA IRRADIATED BY PULSED ELECTRON BEAM IN 5 mm SQUARE AREA

The surface melting is clear from microscopic examination (see Figure 4-3). The initial film is covered with "pyramid" structures (see also Figure 2-6) which are absent after PEB processing. Removal of the material is not possible from weighing measurements. Melting is therefore implied.

The surface structure changes with the fluence used to irradiate the sample. At low fluence ($0.2 - 0.3 \text{ J/cm}^2$) the top of the pyramid structures is melted and appears to flow in a manner which would fill the void space. At higher fluence (0.4 J/cm^2) there are still some peaks and voids visible in the surface. The smooth film shown in Figure 4-3 required 0.5 J/cm^2 . At high fluences, films were damaged.

4.4 CRYSTAL STRUCTURE

Samples of CdTe films deposited on mica, sapphire and silicon were irradiated by a PEB at a fluence sufficient to melt the entire film. Some samples did not adhere to the substrate afterwards (mica), but all were analyzed for crystal structure.

All films were polycrystalline. Analysis determined that all samples processed were deposited prior to modifying the HWE apparatus (see Section 2.4) and were probably not of the correct stoichiometry. The cause of the polycrystalline structure could be the error in composition, and remains uncertain. Experiments were stopped when the EDICT process showed improved crystal structure, and that process was developed more fully with the remaining funds.

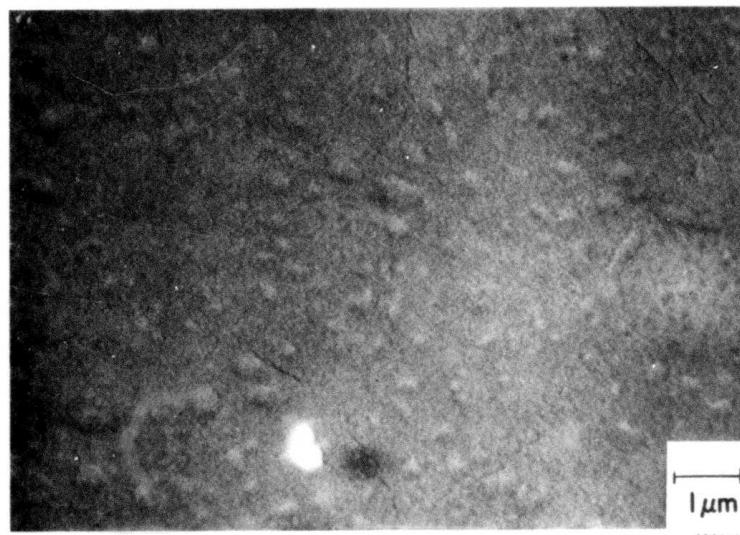
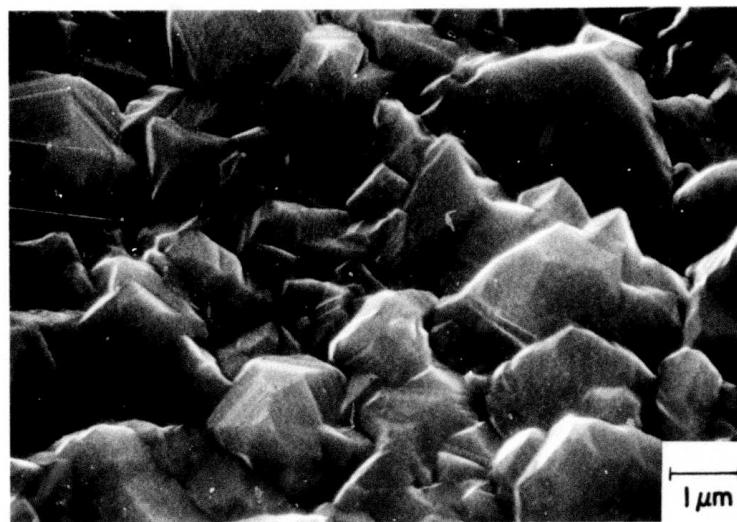


FIGURE 4-3. HWE DEPOSITED CdTe FILM BEFORE (Top) AND AFTER (Bottom) PULSED ELECTRON BEAM IRRADIATION, SHOWING IN SEM MICROPHOTOGRAPH SURFACE POLISHING BY MELTING

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